

# RESERVE COPY PATENT SPECIFICATION

618,895



Application Date: Aug. 14, 1946.

No. 24128/46

Complete Specification Left: Aug. 14, 1947.

Complete Specification Accepted: March 1, 1949.

Index at acceptance:—Class 46, A3.

## PROVISIONAL SPECIFICATION

### Clarification of Coal Washery Effluent

We, JOHN ERIC EDWARDS, of 154, Hillcroft Crescent, Oxhey, Watford, Hertfordshire, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention to be as follows:—

This invention relates to a new and improved process for the clarification of coal washery effluent.

Several coagulating agents are known for clarifying liquids, e.g. sodium aluminate, alum and starch. In addition it is known that silica sols can be used as aids in coagulating the small amount of fine particles normally encountered in raw water. The clarification of coal washery effluent however presents a different problem in that the quantity and size of particles in suspension is frequently large, and most of the known coagulating agents—with the exception of starch—are ineffective or erratic in operation. We have found that soluble silica produces remarkably good results when used in conjunction with aluminium salts or other coagulants at an appropriate pH for the purpose of clarifying coal washery effluent or river water contaminated with such effluent.

According to the present invention, we provide a process for clarifying coal washery effluent which comprises adding thereto a coagulating agent such as aluminium sulphate or sodium aluminate and also soluble silica, and separating the coagulated material. The soluble silica used in this invention is conveniently made from a sodium silicate solution by removing the major part of the  $\text{Na}_2\text{O}$ , e.g. by partial neutralisation with acid or by ion exchange treatment. Such silicate solution may well contain 0.1—3.0%  $\text{SiO}_2$  and 10—50 moles of  $\text{SiO}_2$  per mole of  $\text{Na}_2\text{O}$ . It is convenient to use

sufficient solution to contain 10—100 parts of soluble  $\text{SiO}_2$  per million parts of effluent, and 20—200 parts of aluminium sulphate in the form of a solution per million parts of effluent. The soluble silica and the coagulating agent may be added as solutions, either at the same time or one after the other. The pH of the mixture should generally be adjusted if necessary to about 6—8.

#### EXAMPLE 1.

The coal washery effluent used in this example contained 0.75 gm. of suspended solids per 100 millimetres and had a pH of 7.7. To one million parts of this effluent was added 90 parts of aluminium sulphate and 45 parts of silica sol obtained by partial neutralisation of a dilute solution of sodium silicate with sulphuric acid. This silica sol contained 0.3%  $\text{SiO}_2$  and 1200 parts per million of alkalinity to methyl orange in terms of  $\text{CaCO}_3$ . On settling for less than a minute, the treated effluent yielded a clear liquor of four-fifths of the total volume and with a pH of 6.6. For comparison, the untreated effluent had not settled completely after an hour, and treatment with 80 parts of aluminium sulphate alone gave only incomplete settling after 5 minutes.

#### EXAMPLE 2.

To one million parts of a coal washery effluent containing 2.4 gm. of suspended solids per 100 ml. and having a pH of 7.0, were added 100 parts of lime, 30 parts aluminium sulphate and 30 parts of the silica sol prepared as indicated in the above example. The major portion of the solids settled out in 1 minute, whereas the untreated effluent remained very cloudy after 15 minutes.

Dated the 14th day of August, 1946.

E. A. BINGEN,  
Solicitor for the Applicants.

## COMPLETE SPECIFICATION

## Clarification of Coal Washery Effluent

We, JOHN ERIC EDWARDS, of 154, Hillcroft Crescent, Oxhey, Watford, Hertfordshire, a British Subject, and IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to a new and improved process for the clarification of coal washery effluent.

Several coagulating agents are known for clarifying liquids, e.g. sodium aluminate, alum and starch. It is known that silica sols can be used as aids in coagulating the small amount of fine particles normally encountered in raw water during treatment with aluminium sulphate. It is also known that silica sol may act as a coagulating agent for small amounts of suspended matter present in hard waters containing magnesium. According to Specification 233,842, coal washery effluent can be freed from the finely divided material in suspension by using a coagulating agent or agents such as caustic soda, lime, aluminium sulphate, sodium aluminate, sodium silicate, silicic acid, silica sol, and others. However, silica sol is not *per se* a coagulating agent. Moreover, the production of a clear water from coal washery effluent is more difficult than just the removal of finely divided suspended matter, and most of the known coagulating agents, with the possible exception of starch which is of little or no use in municipal water treatment, are ineffective or erratic for coagulating coal washery effluent. Effluent is discharged in large volumes from coal washeries, and it is objectionable to dispose of because of the large quantity of solids therein and because it is quite black.

We have now found that silica sol containing a small proportion of alkalinity produces remarkably good results when used in conjunction with aluminium salts or other coagulants at an appropriate pH for the purpose of clarifying coal washery effluent or river water contaminated with such effluent.

According to the present invention, we provide a process for clarifying coal washery effluent which comprises adding silica sol and a coagulating agent such as aluminium sulphate or sodium aluminate, and thereafter separating the coagulated material, the silica sol containing one mole of free alkaline  $\text{Na}_2\text{O}$  per 10—50

moles of  $\text{SiO}_2$  for the purpose of stabilising the silica in the correct form. A sol from which all the free alkaline  $\text{Na}_2\text{O}$  has been removed is quite unsuitable. A certain amount of ageing seems to be advantageous in allowing the sol to reach its most effective form.

The silica sol used in this invention is conveniently made from an alkaline silicate solution such as sodium silicate by removing the major part of the caustic alkalinity, e.g. by partial neutralisation with acid or with sodium bicarbonate, or by ion exchange treatment. The silica sol contains 1 mole of free alkaline  $\text{Na}_2\text{O}$  (i.e. caustic alkalinity or hydroxide alkalinity) per 10—50 moles of  $\text{SiO}_2$ , and preferably between 0.1% and 3% of  $\text{SiO}_2$ , because this provides a sufficiently stable solution containing silica in its active form for the present purpose, and the quantity of such solution to be added is a convenient one for large scale operations. It is convenient to use a sufficient solution to contain between 10 and 100 parts, preferably between 20 and 50 parts, by weight of silica sol per million parts of effluent, and between 20 and 200 parts by weight of aluminium sulphate in the form of a solution per million parts of effluent. Obviously these quantities depend *inter alia* on the amount and fineness of the material to be settled, the nature of any other materials such as clay which are present with the fine coal particles, and on plant conditions, but the minimum amount to give satisfactory results in any particular case is readily determined by experiment. The silica sol and the coagulating agent may be added as solutions, either at the same time or one after the other; the best results are often obtained by adding the coagulating agent first and then the soluble silica. The pH of the mixture should generally be about 6—8 because this gives the best results, although the process can be worked at a higher or lower pH.

In making the silica sol, it is essential, if the best results are to be obtained, that appropriate conditions be chosen. We have found that one of the best ways of making it is to add 5% sulphuric acid to an aqueous solution of sodium silicate, at ordinary temperatures, with thorough stirring, to give a solution containing 0.3—5% of  $\text{SiO}_2$  and caustic alkalinity equal to 0.01—0.2%  $\text{Na}_2\text{O}$ . The stirring should be such that there is at no time a high local acid concentration which would cause gel formation. Adequate stirring is usually obtainable by a continuously

operated propellor-type stirrer. The resulting solution is allowed to stand, conveniently for 4-6 hours, after which it is diluted until it contains 0.1 to 3%  $\text{SiO}_2$ .

- 5 Solutions prepared in the manner described above undergo certain changes during this period of standing which affect their value for the present purpose. We have found that the best results are usually obtained after the freshly made solution has stood for one hour and has then been diluted in order to increase its stability, but the optimum period depends *inter alia* upon the concentration of  $\text{SiO}_2$  and the mole ratio of  $\text{Na}_2\text{O}$  to  $\text{SiO}_2$ . The silica sol may also be made from these materials by the continuous addition of the acid and sodium silicate solutions to a stirred batch of the already formed silica sol, with continuous withdrawal of the mixture into a time vessel, and thence into a dilution vessel. With these neutralisation methods, the liquid contains sodium sulphate or other salts formed by the neutralisation, as well as the silica in the form of a sol.

- Alternatively, in making the silica sol, the major part of the caustic alkalinity in a solution of sodium silicate can be converted into carbonate alkalinity, for example by addition of sodium bicarbonate. The mixture is stirred, allowed to stand for a period generally not exceeding a few hours, and then diluted.

- 35 In a third method of making the silica sol, the major part of the caustic alkalinity of a sodium silicate solution may be removed by passing the solution through a bed of cation exchange material which has previously been regenerated with dilute mineral acid. This results directly in a liquid which contains silica of approximately the same concentration as the initial sodium silicate solution, and a much smaller amount of alkaline  $\text{Na}_2\text{O}$  or caustic alkalinity than the original solution. Again, care must be taken to avoid removing all the alkaline  $\text{Na}_2\text{O}$ .

- In one method of carrying out this invention, we add an aqueous solution of aluminium sulphate containing between 20 and 200, or preferably between 50 and 100, parts by weight of  $\text{Al}_2(\text{SO}_4)_3$  to a million parts by weight either of coal washery effluent or of river water contaminated with coal washery effluent, and then add a solution containing 20-50 parts by weight of silica sol obtained as described above, mix intimately and allow to settle. The mixing may be carried out by adding the materials to a vessel and stirring them therein for 2-10 minutes, or by mixing the materials together and adding the mixture to the vessel where they are stirred gently. Water delivered

from the settler is sufficiently clear and colourless for disposal to rivers or for re-use in the washery plant.

The invention is illustrated but not restricted by the following examples, in which the parts are by weight.

#### EXAMPLE 1.

The coal washery effluent used in this example contained 0.75 gm. of suspended solids per 100 millimetres and had a pH of 7.7. To one million parts of this effluent was added a solution containing 90 parts of aluminium sulphate, and a liquor containing 45 parts of silica ( $\text{SiO}_2$ ) obtained by partial neutralisation of a dilute solution of sodium silicate with sulphuric acid, and allowing to stand for one hour and diluting. This silica sol contained 0.3%  $\text{SiO}_2$ , and 240 parts by weight of alkalinity to methyl orange in terms of  $\text{CaCO}_3$  per million parts of liquor (equivalent in this case to 1 mole  $\text{Na}_2\text{O}$  for about 20 moles of  $\text{SiO}_2$ ). On settling for less than a minute, the treated effluent yielded a clear liquor of four-fifths of the total volume and with a pH of 6.6. For comparison, the untreated effluent had not settled completely after an hour, and treatment with 80 parts of aluminium sulphate alone gave only incomplete settling after 5 minutes.

#### EXAMPLE 2.

To one million parts of a coal washery effluent containing 2.4 grams of suspended solids per 100 millimetres and having a pH of 7.0, were added 100 parts of lime, 30 parts of aluminium sulphate and 30 parts of silica as a liquid prepared as described in Example 1. The major portion of the solids settled out in 1 minute, whereas the untreated effluent was still very cloudy even after 15 minutes.

#### EXAMPLE 3.

To one million parts of a coal washery effluent containing 8 grams of suspended solids per 100 millimetres and having a pH of 6.9, were added 90 parts of aluminium sulphate and 45 parts of silica sol in the form of a sol prepared as described in Example 1. On settling for 3 minutes, the effluent yielded a clear liquor for three quarters of its total volume. For comparison, the original effluent when settled for 6 minutes only yielded a fairly clear liquor for one-twentieth of its total volume.

Calcium hydroxide can behave as a coagulating agent in conjunction with silica sol for the purpose of this invention, and we include lime with the common coagulating agents such as alum and sodium aluminate within the scope

of our invention. The amount of calcium hydroxide added may be as much as 1000 parts but is generally 100—200 parts per million parts of effluent.

- 5 Although the process is shown in the examples as a batch operation in which the advantages of the present invention are given in terms of an increased rate of settling, large scale operation  
10 generally involves continuous operation wherein the improvement shown is an increased output from a given filtration or settling plant and/or the delivery of a substantially colourless water instead of  
15 the black-coloured water hitherto customary.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim  
20 is:—

1. Process for clarifying coal washery effluent which comprises adding thereto silica sol and a coagulating agent such as  
25 aluminium sulphate or sodium aluminate, and thereafter separating the coagulated material from the water, characterised in that the silica sol contains 1 mole of caustic alkalinity per 10—50 moles of  
30  $\text{SiO}_2$ , and preferably between 0.1% and 3% of  $\text{SiO}_2$ .

2. Process as claimed in Claim 1 in which the silica sol is obtained by par-

tially neutralising a cold sodium silicate solution with cold dilute mineral acid  
35 while stirring thoroughly, allowing the mixture to stand, and diluting.

3. Process as claimed in Claim 1 in which the silica sol is obtained by adding enough sodium bicarbonate to a cold  
40 sodium silicate solution to convert the caustic alkalinity to carbonate, while stirring, allowing the mixture to stand, and diluting.

4. Process as claimed in any of the preceding claims in which the amount of silica sol added contains between 10 and 100 parts, preferably between 20 and 50 parts, by weight of  $\text{SiO}_2$  per million parts  
50 of coal washery effluent.

5. Process as claimed in any of the preceding claims in which between 20 and 200 parts by weight of aluminium sulphate is added to one million parts of coal washery effluent.  
55

6. Process as claimed in any of the preceding claims in which the coagulating agent is added before the silica sol.

7. Process for clarifying coal washery effluent substantially as hereinbefore described with reference to each of the foregoing examples.  
60

Dated the 14th day of August, 1947.

E. A. BINGEN,  
Solicitor for the Applicants.

Leamington Spa: Printed for His Majesty's Stationery Office by the Courier Press.—1949.  
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. 0d. each (inland) 2s. 1d. (abroad) may be obtained.